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Up converted nanoparticles for photonic applications

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Abstract : The effects of the erbium concentration, crystal hosts and co-dopant on the up converted emission of Er^{3+} in oxide nanocrystals are reported The effects of the Er^{3+} concentration and co-dopant (Yb^{3+}) in the ZrO_2 matrix on the up converted emission are reported. The presence of co dopant (Yb^{3+}) also increases the overall intensity of the up converted emission. A cw diode laser at 975 nm was used as a pump source for resonant sequential excitation of the $^4I_{11/2}$ and $^4F_{7/2}$ levels Green and red up conversion emission at 550 nm and 670 nm were observed from these oxide nanocrystals with 975 nm excitation. The overall intensity decreases with an increasing concentration of erbium in different hosts. In up conversion emission intensity for the same concentration of Er ions, $BaTiO_3$ host showed a highest up conversion emission intensity than that of ZrO_2 and TiO_2 host The emission spectra and the pump intensity dependence of the luminescence intensities confirm that up converted emission in these materials is due to two-photon excited-state absorption (ESA) process.

Keywords . Upconversion, rare-earth, nanoparticle

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1. Introduction

Towards the end of the 20th century and into new millennium, there has been a renaissance in the study of rare-earth doped materials for photonic applications. Nanoparticles, on the other hand, have recently been recognized to hold tremendous potential in the area of photonic applications. Combining the promising optical properties of rare-earth ions and nanoparticles, the study of frequency up conversion processes of erbium in oxide nanoparticles is important. Recently, a great deal of research on IR-to-visible frequency up conversion has been focused to find their potential applications in several areas, such as up conversion lasing, display and two-photon imaging in confocal microscopy [1–4]. Up conversion is a process by which excitation to lower lying levels with low energy radiation results in higher energy emission from higher electronic levels. This process requires the absorption of at least two-photons to provide sufficient energy for the up converted emission to occur. The predominant mechanisms of up conversion in these materials are excited state absorption (ESA) and energy transfer up conversion (ETU). In both of these cases, a simple cw diode laser can be used for the up conversion process, in contrast to expensive mode locked lasers used in two-photon up conversion in organic fluorophore. Efficient up converting nanocrystals of these materials can be good replacement for organic dyes in two-photon confocal-microscope imaging. The efficiency of these materials is dependent on the dynamics of the rare-earth ions and their interactions with the host matrix. This interaction can be a function of the host phase, the dopant concentration, energy migration between the active ions, the statistical distribution of active ions, and site symmetry of the active ions in the host matrix [5, 6].

In the present communication, we report the effect of concentration of erbium ions, oxide hosts and co-dopant on up conversion emission of Er^{3+} in oxide nanoparticles.

2. Experimental section

Here, we use a sol-emulsion-gel process to prepare different oxide particles doped with the Er^{3+} ions [5, 6]. Transmission electron microscopy (TEM) was employed to determine the morphology and the particle size of the resulting powders; the crystalline phases of calcined powders were identified by X-ray diffraction (XRD). The powder XRD patterns of zirconia nanoparticles show the presence of both monoclinic and tetragonal phases for low dopant concentration and cubic at higher dopant concentration. The crystallite size (27–50 nm) varies with the composition. The estimated average crystal sizes of TiO_2 particles (anatase at low temperature and rutile at high temperature) are ~15 nm, 40 nm and >100 nm at 500°, 800° and 1000°C respectively. The estimated average crystal sizes of $BaTiO_3$ particles (cubic phases only) are ~ 30 nm, 50 nm and >80

nm at 700°, 850° and 1000°C respectively. We pressed the particles to form a smooth, opaque flat disk for optical study. The samples were irradiated with a diode laser tuned to 975 nm. A CCD-coupled spectrometer recorded the fluorescence spectra. The absolute fluorescence intensity was measured with a Minolta LS-110 Luminance meter.

3. Results and discussion

Up conversion properties :

A typical energy level diagram for the up converted emission from a sample co-doped with Er^{3+} ions under infrared excitation is shown in Figure 1. The up converted fluorescence spectra of the Er^{3+}: ZrO_2 nanocrystals in different concentrations of Er^{3+} are shown in Figure 2. A significant drop in the overall intensity and a change in the spectral nature of these bands are observed with an increasing concentration of Er^{3+} ions. The relative increase in intensity of red emission with respect to the intensity of green emission was observed with an increasing concentration of erbium. The mechanism of the up converted emission of Er^{3+} has been well established in the literature [4]. The diode-laser wavelength matches the absorption transition between the ground state, $^4I_{15/2}$, and the excited level $^4I_{11/2}$. After first-level excitation, the same laser pumps the excited atom from the $^4I_{11/2}$ to the $^4F_{7/2}$ level. Subsequent nonradiative relaxation populates the $^4S_{3/2}/^2H_{11/2}$ and the $^4F_{9/2}$ levels. Bright green (550 nm) and red (675 nm) emission were observed due to the transitions $^4S_{3/2}$ $^4I_{15/2}$ and $^4F_{9/2}$ $^4I_{15/2}$, respectively. At low concentration, the erbium ions are usually randomly distributed in the host lattice but at higher concentration, some of the Er^{3+} ions have a closer nearest neighbor than others and concentration quenching can occur. At low dopant concentration, the $^4S_{3/2}/^2H_{11/2}$ levels decay mostly radiatively to $^4I_{15/2}$. Therefore, the green emission has a higher intensity. It is reported that at a higher concentration, the luminescent lifetime of $^4S_{3/2}/^2H_{11/2}$ levels are shortened as a result of the cross-relaxation (CR) processes between ($^2H_{11/2} \rightarrow$ $^4I_{9/2}$) and ($^4I_{15/2}$ $^4I_{13/2}$) transitions as shown in Figure 1. This cross-relaxation process is dominant at higher concentration of Er^{3+} ions. Therefore, quenching of emission takes place at higher concentrations of erbium ions [5].

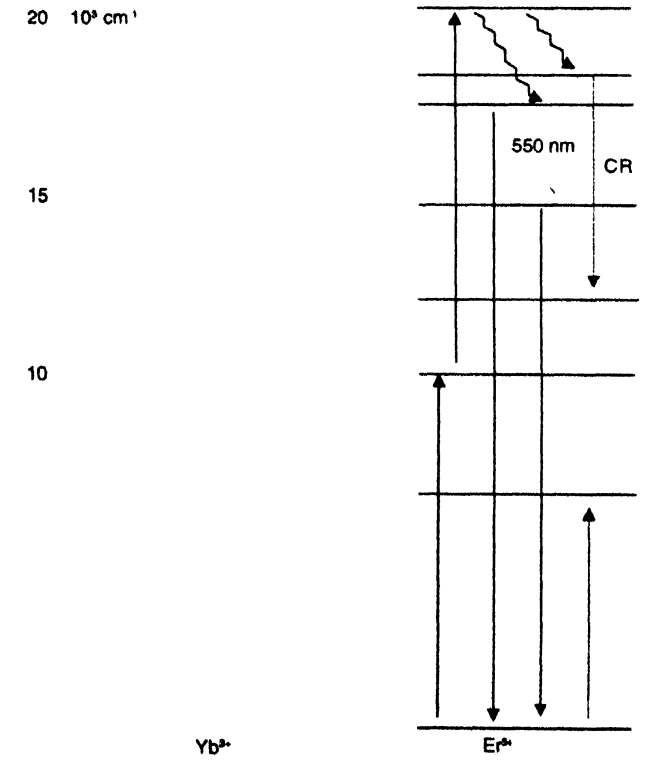

Figure 1. The energy level diagram for Yb^{3+} and Er^{3+} ions under infrared excitation.

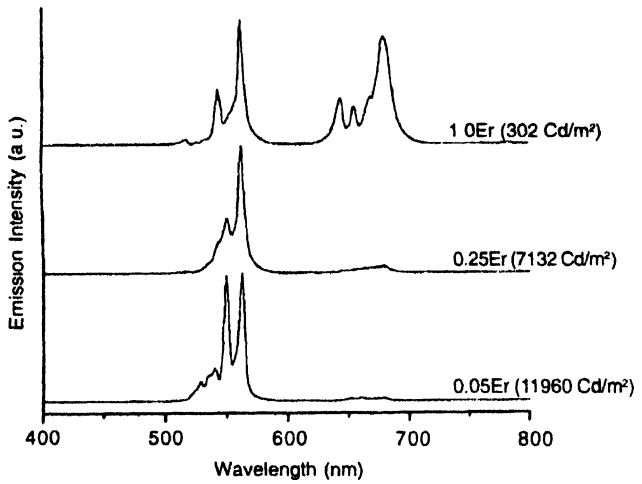

Figure 2. Up converted emission spectra of different concentrations of Er^{3+} in ZrO_2 nanoparticles heated at 1000°C.

The up conversion luminance values for 0.25 mol% Er^{3+} : ZrO_2 and 0.25 mol% (Er^{3+}+ Yb^{3+}) : ZrO_2 nanoparticles sintered at 1000°C are 7132 Cd/m² and 8850 Cd/m² respectively. The mechanism for this up conversion is energy transfer from Yb^{3+} ($^2F_{5/2}$) to Er^{3+} ($^4I_{11/2}$). The ET from Yb^{3+} ($^2F_{5/2}$) to Er^{3+} ($^4I_{11/2}$) depends on the Yb^{3+} concentration, *i.e.* the transfer process depends upon the donor and acceptor concentrations. During the lifetime of the $^4I_{11/2}$ level a second photon is absorbed by Yb^{3+} and energy transferred to Er^{3+}. The Er^{3+} is now raised from $^4I_{11/2}$ to $^4F_{7/2}$. The possible channels for the green and red up conversion luminescence are given below :

$$^2F_{5/2}(Yb^{3+}) + {}^4I_{11/2}(Er^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^4F_{7/2}(Er^{3+}).$$

The $^4F_{7/2}$ (Er^{3+}) state decays nonradiatively to the $^4S_{3/2}/^2H_{11/2}$ and $^4F_{9/2}$ (Er^{3+}) levels. The green emission is observed from the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition while the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition produces red emission. This is also confirmed [5] by the observed increase in overall emission intensity in the presence of Yb^{3+} with Er^{3+}. The up conversion luminance values for the 0.25 mol% Er^{3+} : TiO_2 nanoparticles sintered at three different temperatures are 97.35 Cd/m², 207.5 Cd/m² and 120.5 Cd/m² at 500°, 800° and 1000°C sintering temperatures respectively. The up conversion luminance values in Er^{3+} : $BaTiO_3$ nanoparticles sintered at 1000°C are 17130 Cd/m², 9487 Cd/m², 1653 Cd/m² and

540 Cd/m^2 for 0.25, 1.0, 2.5 and 10–mol% Er^{3+} respectively. The up conversion luminance values are 120.5 Cd/m^2, 7132 Cd/m^2 and 17130 Cd/m^2 for 1000°C heated 0.25 mol% Er^{3+} doped TiO_2, ZrO_2 and $BaTiO_3$ samples respectively [5, 6]. These results can be explained from phonon energies of this host [7].

The variations of the fluorescence intensity of the green and red emission *versus* pump intensity in various compositions are plotted in Figure 3. For two photon an ETU/ESA up conversion process, the fluorescence intensity should be related to the pump intensity by the following equation [5, 6]

$$I_f = \frac{KI_n^2}{\left(A + BI_p + CI_p^2\right)}, \quad (1)$$

where, all the coefficients are always positive. I_f is the up converted fluorescence intensity and I_p is the pumping intensity. K is a constant that depends on collection geometry and the Er^{3+} density in the sample. A, B, and C are constants related to the transition probabilities, and the absorption cross-section of

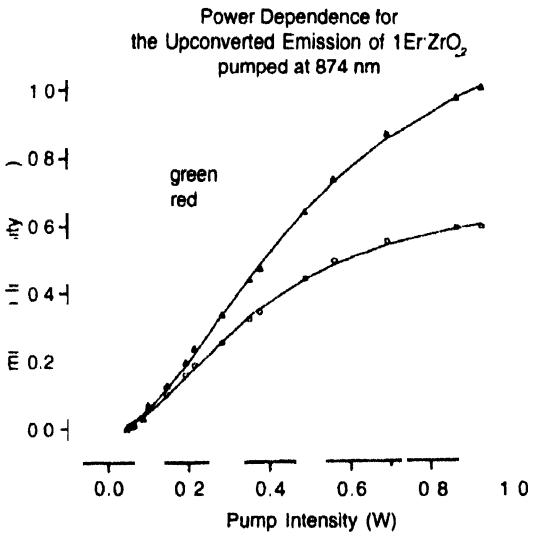

Figure 3. Variation of red and green up converted emission intensities with pump power for 1.0 Er^{3+} : ZrO_2 sample.

the involved transitions. It can be seen in Figure 3 that eq. (1) fits excellently to all sets of experimental data. These results confirm that the up conversion in all these materials is due to two-photon ESA process.

4. Conclusions

We have shown that the overall up conversion luminescence intensity decreases with an increasing concentration of the Er^{3+} ions in different oxide matrix. The Yb^{3+} ions, which act as a sensitizer, also enhance the up conversion luminescence under infrared excitation. In up conversion emission intensity for the same concentration of Er ions $BaTiO_3$ host showed a higher up conversion emission intensity that the ZrO_2 and TiO_2 host. We have also confirmed that the up conversion process in all these materials results from two-photon ESA processes.

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